Tailoring of Corrosion-Resistant Tungsten Alloys by Sputtering(スパッター法による耐食タングステン合金の創製)

W-Cr alloys are not exceptional, and hence the W-Cr alloys cannot be amorphized. However, the amorphous structure for both the sputter-deposited W-Ta and W-Nb alloys is formed. On the other hand, the amorphous structure for the W-Zr and W-Ti alloys is successfully prepared in a wide composition range.

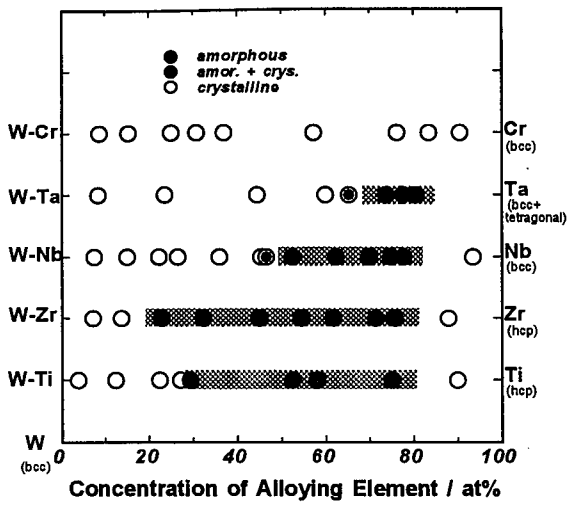

Figure 1. The structure of the sputter-deposited tungsten alloys identified by X-ray diffraction.

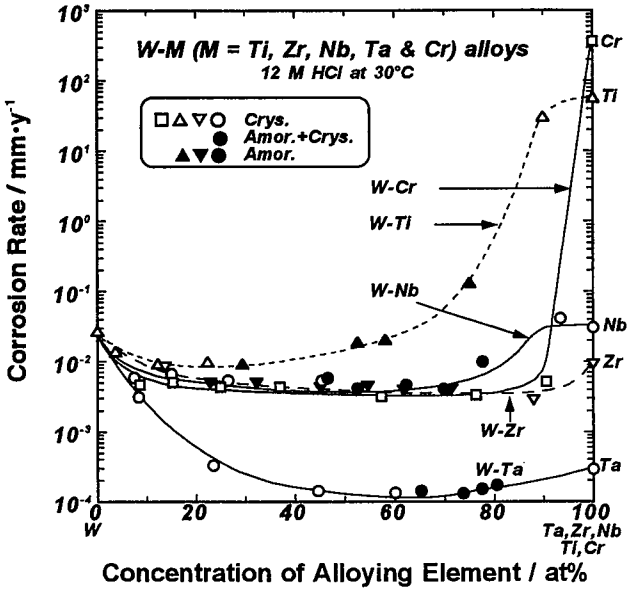

Figure 2. Changes in corrosion rates of the sputter-deposited tungsten alloys in 12 M HCl at 30°C as function of concentration of alloying element

The apparent grain size of the amorphous tungsten alloys was of the order of about 1-2 nm, which is only a little larger than the size of atom groups supposed to exist in liquid metals. The apparent grain size of the other tungsten alloys was of the order of 6-20 nm. Consequently, the sputter-deposited tungsten alloys consist of single-phase amorphous or nanocrystalline solid solutions.

The corrosion rates of the tungsten alloys are estimated from the weight losses after immersion in concentrated hydrochloric acids at 30°C for about 1 week. As shown in **Fig. 2**, all the sputter-deposited tungsten alloys, which are composed of either an amorphous or a nanocrystalline single phase, show lower corrosion rates than those of alloy-constituting elements in 12 M HCl at 30°C. It is already mentioned that the apparent grain size of the crystalline tungsten alloys is less than 20 nm, and hence the corrosion rate of the sputter-deposited tungsten alloys is not greatly affected by the structure of the alloys. All the sputter-deposited tungsten alloys are spontaneously passive in concentrated hydrochloric acids at 30°C.

2.2 Passive films formed on spontaneously passivated tungsten alloys: The composition of the passive film gives an important information about the stability and protectiveness of the passive films. Therefore, change in the surface composition of the tungsten alloys is analyzed by X-ray photoelectron spectroscopy (XPS) including the angle-resolved measurements to clarify the high corrosion resistance of the tungsten alloys in concentrated hydrochloric acids at 30°C. **Figure 3** shows a typical example of the change in the surface composition as a function of alloy tantalum content for the W-Ta alloys. Tantalum is rich in both the air-formed film and the passive film for all W-Ta alloys with respect to alloy composition, while the reverse is seen for the underlying alloy surface. Furthermore, the compositions of films formed on the spontaneously passivated W-Ta alloys are almost independent of the immersion time. Accordingly, very

stable tantalum-rich passive films are formed on the W-Ta alloys within 1 h immersion in 12 M HCl. Similarly, zirconium-concentrated films formed on the spontaneously passivated W-Zr alloys. On the other hand, tungsten is concentrated in the films formed on the spontaneously passivated W-Ti, W-Nb and W-Cr alloys as a result of preferential dissolution of relatively less protective alloying component-concentrated air-formed films in hydrochloric acids. The angle-resolved XPS measurement revealed that both cations of the binary tungsten alloys are distributed homogeneously in the films formed on spontaneously passivated tungsten alloys in hydrochloric acids, although there is a small concentration gradient of cations for W-Ta and W-Zr alloys.

Knowledge of any electronic interaction between the alloying constituents of the binary alloys would give important information about the structure of the film. In this work, it is found that binding energies of core electrons in the surface films formed on the W-Ti, W-Zr, W-Nb, W-Ta and W-Cr binary alloys, that is, W^{4+} $4f_{7/2}$ and Ti^{4+} $2p_{3/2}$; W^{4+} $4f_{7/2}$ and Zr^{4+} $3d_{5/2}$; W^{4+} $4f_{7/2}$ and Nb^{5+} $3d_{5/2}$; W^{4+} $4f_{7/2}$ and Ta^{5+} $4f_{7/2}$, and W^{4+} $4f_{7/2}$ and Cr^{3+} $2p_{3/2}$ electrons, respectively, changed continuously with cationic compositions of the passive films. It is, therefore, concluded that the passive films formed on these binary tungsten alloys are composed of homogeneous double oxyhydroxides. Consequently, high corrosion resistance of binary tungsten alloys is based on the formation of passive double oxyhydroxide films composed of both alloy component cations. These films have higher protectiveness and stability than those of passive oxyhydroxide films of alloy component elements.

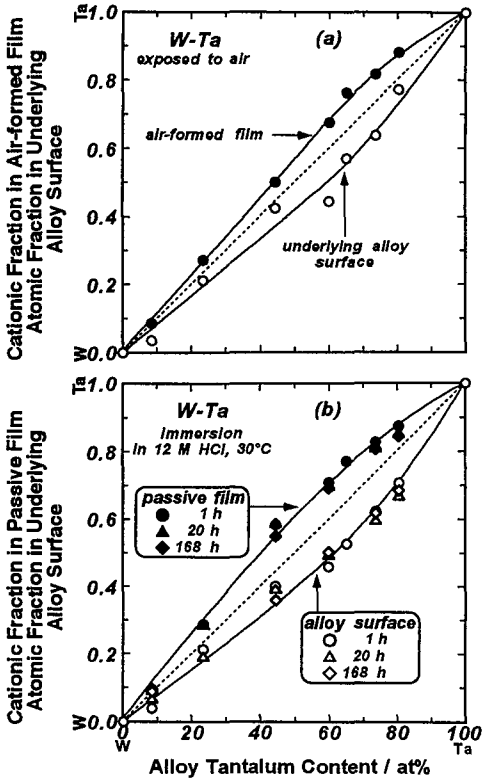

Figure 3. Changes in surface compositions for W-Ta alloys (a) after air exposure of mechanically polished specimens and (b) after immersion in 12 M HCl at 30°C.

2.3 Potential dependence of the surface of tungsten alloys: The potential dependence of the surface composition of the passive films formed on the tungsten alloys is studied to clarify mechanisms of the passivity as well as the pitting resistance of the sputter-deposited tungsten alloys in concentrated hydrochloric acids. The change in the surface composition of the anodic passive films formed on the tungsten alloys after potentiostatic polarization for 1 h in concentrated hydrochloric acids at 30°C were analyzed by XPS.

The passive film composition of tungsten alloys changes mainly in three regions, that is, the active regions of alloying elements, the passive and transpassive regions of alloying elements, and the region where oxidation of W^{4+} to W^{6+} occurs. If the tungsten alloy is polarized near the active potential regions of alloying element, a significant enrichment of tungsten is observed. Consequently, tungsten is remarkably concentrated in the passive films formed on W-Ti and W-Cr alloys near the active regions of titanium and chromium, respectively. If tungsten is significantly concentrated in the passive films by the preferential dissolution of alloying element ions from air-formed films, tetravalent tungsten is the main tungsten species

at the open circuit potential. When tetravalent tungsten is oxidized to hexavalent tungsten by anodic polarization, the concentration of tungsten ions slightly decreases with increasing the cationic fraction of alloying element in the passive films formed on W-Ti, W-Nb, W-Ta and W-Cr alloys.

Anodic polarization leads to film thickening of the tungsten alloys in concentrated hydrochloric acids at 30°C. Both cations of the binary tungsten alloys contribute for the anodic film thickening. The main contributor among tungsten ions for the anodic film thickening of the tungsten alloys is W^{6+} ions, because a relatively stable and sparingly soluble W^{6+} ions increase remarkably in the anodic passive film in the potential region where film thickening is remarkable in hydrochloric acids.

2.4 Role of alloying elements in the passivation behavior of sputter-deposited tungsten alloys: A comparison of beneficial effects of alloying elements in enhancing the corrosion resistance of tungsten alloys has been carried out by corrosion tests in concentrated hydrochloric acids and by the surface analyses.

Among W-50M (M = Ti, Zr, Nb, Ta and Cr) alloys the W-50Ta alloy has the highest corrosion resistance. The corrosion resistance decreases in the order of W-50Cr, W-50Zr, W-50Nb and W-50Ti alloys. All these alloys possess higher corrosion resistance than alloy component elements.

The thick air-formed films on W-Ta and W-Zr alloys are stable and protective in 12 M HCl and are responsible for spontaneous passivation. Spontaneous passivation of W-Cr alloy takes place due to the presence of the stable and protective air-formed film. The surface films formed on W-Ti and W-Nb alloys by air exposure are not highly stable in concentrated hydrochloric acids, and conversion of the air-formed film to the passive film takes place due to preferential dissolution of titanium and niobium. The conversion of the air-formed film to the passive film on W-Nb alloys having higher corrosion resistance than W-Ti alloys occurs relatively slowly.

3. CONCLUSIONS

Direct current (D. C.) magnetron sputter deposition technique is applied to tailor highly corrosion-resistant tungsten alloys. The structure of tungsten alloys thus prepared is characterized by X-ray diffraction (XRD) and their corrosion behavior is studied in concentrated hydrochloric acids at 30°C by immersion test, electrochemical measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The main conclusions are as follows:

1. The sputter deposition is significantly effective technique to tailor a new series of nanocrystalline or amorphous single phase solid solutions of binary tungsten alloys over a wide composition range.

2. All the sputter-deposited tungsten alloys, except the W-90Ti alloy, are spontaneously passive in concentrated hydrochloric acids at 30°C. Titanium, zirconium, niobium, tantalum and chromium metals act synergistically with tungsten in enhancing the corrosion resistance so as to show the lower corrosion rates than the corrosion rates of the alloy-constituting elements in concentrated hydrochloric acids.

3. The quantitative surface analysis by XPS clarifies that the higher corrosion resistance of the spontaneously passivated tungsten alloys than those of alloy-constituting elements is based on the formation of new passive double oxyhydroxide films composed of both alloy component cations. These films have higher protectiveness and stability than those of passive oxyhydroxide films of alloying elements.

Outline of this study

This thesis consists of seven chapters as follows:

In **Chapter 1**, background, previous studies and objectives of this study are discussed. The great advantage of the sputtering technique for the development of novel alloys having superior corrosion resistance is described in this chapter. Previous investigations on the sputter-deposited corrosion-resistant amorphous or nanocrystalline alloys are surveyed to depict the reason for tailoring the corrosion-resistant binary tungsten alloys by sputtering.

In **Chapter 2**, experimental methods are described in detail.

Structures of the sputter-deposited W-Ti, W-Zr, W-Nb, W-Ta and W-Cr alloys are identified by X-ray diffraction in **Chapter 3**. The apparent grain size and the change in the lattice spacing of the alloys are also discussed. The estimated corrosion rates of the sputter-deposited tungsten alloys including alloy-constituting elements from weight losses of specimens after immersion in concentrated hydrochloric acids at 30°C are shown in this chapter. The electrochemical behavior of the tungsten alloys is studied to clarify their higher corrosion resistance in concentrated hydrochloric acids at 30°C, open to air.

In **Chapter 4**, the results obtained from XPS analysis of spontaneously passivated tungsten alloys are elucidated. The surface analyses of the passive films on the tungsten alloys give a crucial information for a better understanding of the effect of alloy-constituting elements in the corrosion behavior of the binary alloys. Particular attention is paid to the change in the composition and structure of films formed on the spontaneously passivated tungsten alloys.

The change in the surface composition by potentiostatic polarization of the tungsten alloys is elucidated in **Chapter 5**. Particular attention is paid to the change in the oxidation state of tungsten by anodic polarization, because distribution of different oxidation states of tungsten affects the stability of the anodic passive films and film thickening of the tungsten-base alloys in concentrated hydrochloric acids.

Comparative roles of individual alloying elements in enhancing the high corrosion resistance of the tungsten alloys are discussed with some examples in **Chapter 6**.

Conclusions of this thesis are summarized in **Chapter 7**.

審 査 結 果 の 要 旨

本論文は、スパッター法によって、耐食金属同士からなるタングステン合金の作製を試み、高耐食性を備えた単相固溶体合金の作製に成功し、その高耐食性の原因を明かにした研究の内容をまとめたものであって、全編7章よりなる。

第1章は緒論であり、本研究の背景と目的を述べている。

第2章では、実験方法を述べている。

第3章では、W-Ti、W-Zr、W-Nb、W-TaおよびW-Cr合金を作製し、その構造と耐食性を調べ、W-Ti、W-Zr、W-NbおよびW-Ta合金には中間の組成でアモルファス単相が生じ、その他の組成の合金はナノ結晶粒からなるbcc単相固溶体であって、いずれの合金も 12 M HCl 中で自己不働態化して高耐食性を示し、合金構成元素単体より高い耐食性を備えていることを見いだしている。

第4章では、これらの合金の高耐食性の原因を明かにするため、12 M HCl 中で生じる不働態皮膜の組成と構造をX線光電子分光法を用いて調べ、タングステンに生じる不働態皮膜を構成するW^{4+}イオンと合金元素のイオンを共に含む複オキシ水酸化物不働態皮膜が生じることが高耐食性の原因であることを見いだしている。

第5章では、タングステン合金はアノード分極しても過不働態溶解を受けないことに着目し、アノード電位での耐食性を明かにするため、12 M HCl 中でアノード分極によって生じる不働態皮膜の組成と構造をX線光電子分光法を用いて調べ、W^{6+}イオンと合金元素のイオンがほぼ均一に分布するオキシ水酸化物不働態皮膜が生じることが高耐食性の原因であることを見いだしている。

第6章では、タングステンに添加する5種類の元素の役割を比較し、 最も耐食性を向上させるタンタルを始めジルコニウムおよびクロムを含む合金では、大気中で生じる複オキシ水酸化物皮膜が 12 M HCl 中ですらきわめて安定であって高耐食性を示すこと、チタンおよびニオブを含む合金では大気中で生じる複オキシ水酸化物皮膜からチタンやニオブが 12 M HCl 中に溶解して安定な不働態皮膜に変わることを明かにしている。

第7章では、本研究で得られた成果を総括している。

以上要するに、本論文は、タングステンと他の耐食金属からなる単相合金の作製に成功し、これらが12 M HCl 中で自己不働態化して高耐食性を示すことを明かにし、自己不働態化皮膜の組成と構造を調べて高耐食性の原因を検討したものであって、材料物性学の発展に寄与するところ少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。